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IR absorption spectra of liquid crystals confined in the channels of macroporous silicon

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Abstract. Macroporous silicon, possessing a regular triangular pattern of air or liquid crystal (LC) encapsulated pores, was studied by FTIR spectroscopy. It was found that rod-like ferroelectric LC molecules are oriented along the pore axis and discotic LC columns are perpendicular to it. Strong intensity enhancement of the low-frequency vibrational bands was detected for both LC's infiltrated in the matrix of porous silicon and were assigned to the photonic confinement effects.

1. Introduction

Porous systems such as artificial opals, porous semiconductors, etc. have recently attracted a great attention. Of a special interest are regular porous structures, which can form photonic band gap of different dimensions. The idea to infiltrate porous systems with liquid crystals (LC) in order to control the position of their photonic band gap due to the change of the LC refractive index was suggested in [1, 2]. Today only first steps in the study of infiltration process and LC behavior in confined geometry of macroporous silicon have been done in [3]. In this paper we applied infrared spectroscopy to investigate the alignment of liquid crystal molecules of different shape in the macroporous silicon matrix.

2. Experimental

Macroporous silicon (ma-PS) under this study (Fig. 1(a)) is a material with a system of a regular cylindrical pores of 3–4.5 μm diameter and 200–250 μm depth, arranged in triangular lattice of 12 μm period. The pores were etched in HF solution under the back side illumination [4]. Two different types of liquid crystal materials were used in this study (see Fig. 1(b)): the commercial ferroelectric liquid crystal (FLC) mixture SCE-8 and the triphenylene based discotic liquid crystal (DLC) H7T-NO₂. The liquid crystals were infiltrated by capillary effect at temperature approximately 10°C above the transition temperature to the isotropic phase.

Fourier transform infrared (FTIR) measurements were performed with the help of Digilab FTS60A spectrometer in the wavenumber range of 450–4000 cm^{-1} . The alignment of LCs in porous silicon matrix was deduced from the comparison of the relative intensities and the position of different vibrational bands for the bulk liquid crystals and for that infiltrated into the pores. For this purpose a number of liquid crystalline cells with different type of alignment (homeotropic and planar) have been prepared. The relative intensities were compared for a number of vibrational bands with transition dipole moment oriented (i) along or perpendicular to the long molecular axis for rod-like molecules of the ferroelectric LC and (ii) parallel or perpendicular to the core for disk-shaped molecules in the case of the discotic LC. Porous matrix filled with LC had a fixed position with the respect to the incident light: normal to the wafer surface, i.e. along the pore axis.

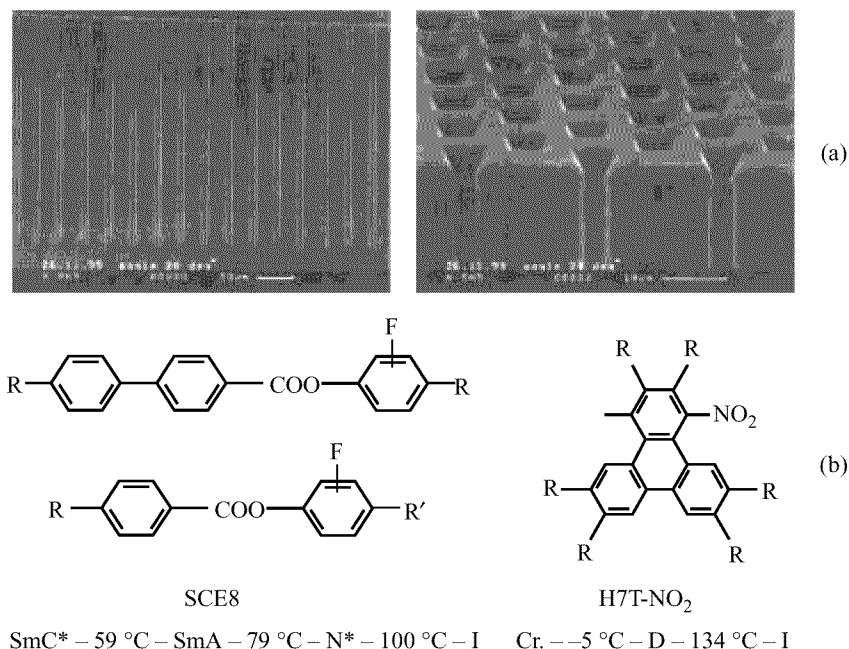


Fig. 1. Materials properties. (A) SEM image of macroporous silicon matrix (side view (a) and top view (b)), used to infiltrate with the liquid crystals; (B) Structure formulas and the phase sequences of ferroelectric liquid crystalline mixture SCE8 and the tryphenylene based discotic liquid crystal H7T-NO₂ ($R = \text{OC5H11}$).

3. Results and discussion

Figures 2(a,b) show the vibrational bands of discotic liquid crystal for homeotropic and planar alignment of molecules in liquid crystalline cell and in the porous matrix. It should be noted that the alignment of discotic liquid crystals is usually considered with the respect to the column axis, which is in general perpendicular to the core plane. The alignment of DLC is planar with respect to the substrate plane (or homeotropic with respect to the pore surface) (see Fig. 3). The most convincing result of this comparison is shown by behavior of the alkyl chain vibrations. In particular, as one can see from Fig. 2(a), the relative intensities of CH₃ symmetric (at $\sim 2871 \text{ cm}^{-1}$) and asymmetric (at $\sim 2959 \text{ cm}^{-1}$) stretching vibrations are different from the corresponding CH₂ stretching vibrations (at 2861 and 2934 cm^{-1}) for planar and homeotropic alignment of DLC cells. The spectrum of H7T-NO₂ in ma-PS is similar to that for the planar alignment of DLC cell in the same frequency range. Another argument is given in Fig. 2(b), where range the frequency $650\text{--}800 \text{ cm}^{-1}$ is shown. Here the CH₂ rocking vibration shows up at 724 cm^{-1} for H7T-NO₂ in porous matrix and in ZnSe cell with planar alignment while for ZnSe cell with homeotropic alignment the position of this band is at $\sim 733 \text{ cm}^{-1}$. This shows that the alkyl chain is in all trans configurations for the planar alignment of DLC molecules [5]. The intensities ratio ($R = A^{\parallel}/A^{\perp}$) obtained for C-C aromatic stretching vibration at 1510 cm^{-1} (parallel to the core) and C-H aromatic out of plane vibrations at 824 cm^{-1} equal 16 for the planar cell, 8 for the homeotropic cell and 1.2 for ma-PS. Finally from all aforementioned data it is obvious that the behavior of H7T-NO₂ in ma-PS is exactly coincide with that for the

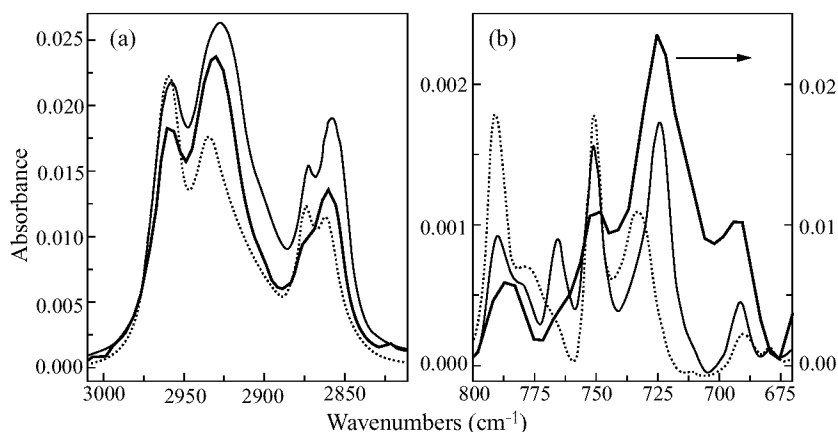


Fig. 2. FTIR spectra of H7T-NO₂ discotic liquid crystal infiltrated into porous silicon (heavy solid line) and contained in ZnSe cells with planar (thin solid line) and homeotropic (dashed line) alignment. (Note the different scale for the heavy line at plot (b) and that the absorbance for DLC cells reduced for planar cell by factor 50 and for homeotropic cell by factor 45 for convenience of presentation).

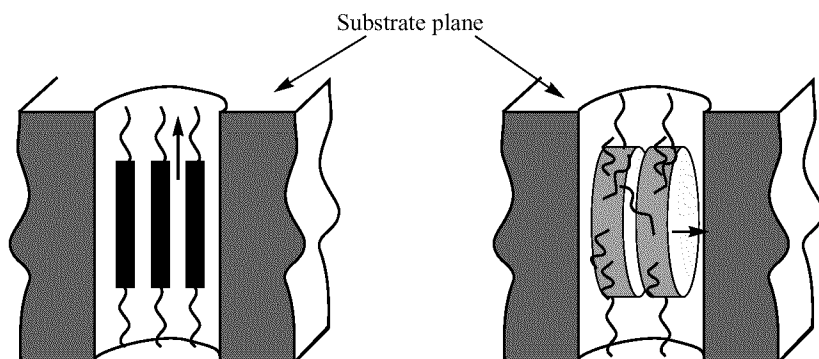


Fig. 3. Orientation of discotic (a) and ferroelectric (b) liquid crystal molecules in macroporous silicon matrix.

planar alignment of DLC cell. This is in accordance with the conclusions on the higher stability of homeotropic alignment for discotic liquid crystals [5].

IR spectra of SCE-8 infiltrated into porous silicon matrix show that the relative intensities of parallel and perpendicular bands in this case are close to that observed for the bulk LC cell with homeotropic alignment. This mean that the alignment of ferroelectric liquid crystal in confined porous silicon matrix is homeotropic with respect to the substrate's plane. This result coincides with the alignment obtained for nematic LC in macro and microporous silicon [6]. One could predict this kind of orientation if consider the alignment of rod-like molecules with respect to the surface of the pores. The alignment is planar with the respect to the pore surface. This type of alignment is typically observed for rod-like molecules on different untreated surfaces, including crystalline silicon substrate [7]. Only a special surface treatment or coating of the substrate surface by a surfactant may provide a homeotropic alignment of LC's formed of rod-like molecules.

In course of these investigation we found strong intensity enhancement of the low-

frequency vibrational bands (in $600\text{--}900\text{ cm}^{-1}$ region) for both types of liquid crystals (note the different scale for this region shown in Fig. 2(b)). This becomes in particular noticeable from a comparison of the intensities ratio shown above for parallel and perpendicular bands. As was already mentioned these intensities ratio appears much smaller than even obtained for both LC cells with homeotropic alignment. Moreover this enhancement is observed for all vibrational bands (parallel and perpendicular ones) show up for the wave lengths comparable with the lattice constant of the photonic crystal ($12\text{ }\mu\text{m}$). This enables us to consider the effect as being due to the light localization in the hole core of the structure as it takes place in the fibers with photonic band gap cladding [8]. Similar effects of absorption enhancement has been observed by Alieva et al. [9] for the species in the microcavity of 1D photonic structure.

4. Conclusion

We found that channel walls affect the orientation of LC molecules so that the column axis of discotic LC is perpendicular to them, and the long side of the rod-like molecules of ferroelectric LC is aligned along the channel walls. We observed the effect of photonic medium influence on the vibration properties of the LC molecules inside the matrix of macroporous silicon and suppose it to be related to Purcell type confinement effect.

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